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An Approximate Rate Equation for the Activated Adsorption

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21. An Approximate Rate Equation for the Activated Adsorption.

Shinjiro Kodama and Noriaki Kadota.

Though the rate formula formerly proposed by us for the activated adsorption was based on the assumption of the nonuniform surface, the equation derived there⁽¹⁾ was that of a bimolecular type. And this rate formula was found to be unsufficient for the later precise experiments.

In the present paper, two types of adoptions are assumed, i. e.

$$\frac{dx_1}{dt} = K_1' p (A_1 - x_1) - k_2' x_1, \quad (1)$$

$$\frac{dx_2}{dt} = K_2 p (A_2 - x_2)^2 - k_2 x_2^2, \quad (2)$$

and

$$\frac{dx}{dt} = \frac{dx_1}{dt} + \frac{dx_2}{dt} \quad (3)$$

where x_1, x_2 : amount of adsorbed gas,

K_1', K_1 : rate constants of the adsorption,

k_2', k_2 : rate constants of the reverse processes,

A_1, A_2 : numbers of sites of types (1) and (2) respectively, which are mutually independent.

The adsorption of the type (1) is considered to be very rapid because of the low activation energy and to have attained the equilibrium by the time of the observation beginning. If we assume the completeness of the clean-up of the surface before the experiment, the integration of the rate equation will be given without any abbreviation as follows:

$$x = \frac{A_1 K_1' p}{k_2' + K_1' p} + \frac{A_2 \sqrt{K_1 p}}{\sqrt{K_1 p} + \sqrt{k_2} \coth A_2 \sqrt{K_1 k_2 p t}} \quad (4)$$

The equation (4) can not easily be verified when the surface is not completely cleaned up, as is the case with the ordinary desorption process. Since we know the influence of the reverse process is very small on the adsorption process, we can neglect the second term in the equation (2) and put $x_2 = (x_2)_0$ for $t=0$. Then the rate equation is given by

$$x = (x_1)_{eq} + \frac{A_2 (A_2 - (x_2)_0) K_1 p t + (x_2)_0}{1 + (A_2 - (x_2)_0) K_1 p t} \quad (5)$$

where the first term of the equation (4) is substituted by $(x_1)_{eq}$. From the two sets of the observed values (t_1, x_1) and (t_2, x_2) , we can introduce the following relation.

$$\frac{x_2 - x_1}{t_2 - t_1} = \frac{(A_2 - (x_2)_0)^2 K_1 p}{\{1 + (A_2 - (x_2)_0) K_1 p t_1\} \{1 + (A_2 - (x_2)_0) K_1 p t_2\}}$$

As the limiting case, we get

$$\frac{dx}{dt} = \frac{(A_2 - (x_2)_0)^2 K_1 p}{\{1 + (A_2 - (x_2)_0) K_1 p\}^2} \quad (6)$$

which has an implicit expression as to x . Putting $(A_2 - (x_2)_0) K_1 p = a$ and $(A_2 - (x_2)_0) = \beta^2$, we can rewrite the equation (6) as,

$$\beta \left(\frac{dx}{dt} \right)^{-1/2} = 1 + at \quad (7)$$

which corresponds to the linear relationship between $\left(\frac{dx}{dt} \right)^{-1/2}$ and t . This relation was verified on the results of the authors for the adsorption of H_2 on Ni⁽²⁾ and ⁽³⁾ Cu, carried by kieselguhr respectively, and those of Soller and others⁽⁴⁾. The test of the equation showed that it was correct for the results observed under comparatively low pressure, e. g. 1/50 atms. pressure. The equation, however, was found not to hold under higher pressures.

This might be probably of the dependence of each elementary process or so remarkable inter-actions between the processes (1) and (2) that can not be neglected.

22. Studies on the Rate of Reaction of CH_4 and CO_2 . (II)

The Reaction of H_2 and CO_2 .

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The rate of reaction of CO_2 and H_2 , one of the reactions which might occur in the thermal reaction of CH_4 and CO_2 , was measured by the flow method under the atm. pressure. Under the condition of the reaction temp. 1210–1131°K and the contact time 0.1–1.0 sec., the effects on the degree of conversion in compliance with the alteration of ratio of CO_2/H_2 were observed and the following results were obtained.

1. This reaction is heterogeneous because the rate of reaction is accelerated in the reaction vessel when packed with some quartz fragments.

2. Under the constant velocity of total flow, the reaction rate seems to increase according to the increase of CO_2 content, while there is no apparent change in the range of the ratio CO_2/H_2 larger than unity.

3. When the velocity of CO_2 flow is constant, the conversion of CO_2 decreases according to the increase of H_2 quantity, but when the velocity of H_2 flow is constant, the conversion of H_2 increases, though slightly, as CO_2 increases in spite of shortening the contact time.